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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 05/18/95	3. REPORT TYPE AND DATES COVERED Final Report 7/1/91-6/30/94	
4. TITLE AND SUBTITLE Block Copolymer Ionomers			5. FUNDING NUMBERS N00014-56-J-0011	
6. AUTHOR(S) R. A. Weiss				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Institute of Materials Science University of Connecticut 97 N. Eagleville Road Storrs, CT 06269-3136			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 N. Quincy Street Arlington, VA 22217-5000			10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Distribution Unlimited			12b. DISTRIBUTION CODE	
<div style="text-align: center;">  </div>				
13. ABSTRACT (Maximum 200 words) Three types of block copolymers were used to prepare block copolymer ionomers: (1) a triblock copolymer of styrene and ethylene-co-butylene (SEBS) obtained commercially and diblock and triblock copolymers of styrene and ethylene-co-propylene (SEP and SEPS) that were synthesized by anionic polymerization of styrene and isoprene followed by hydrogenation of the polyisoprene block. The styrene content of the SEBS was 30% (wt); the styrene content of the SEP and SEPS was varied from 10-50% to obtain spherical, cylindrical or lamellar microstructures. The styrene blocks were sulfonated to 0-18 mol% with acetyl sulfate, and the free acid derivative and the Na ⁺ and Zn ²⁺ salts were prepared. The block copolymer ionomers exhibited two different levels of microphase separation: (1) a block microstructure with a characteristic dimension of the order of 10-20 nm and an ionic microstructure of the order of 2-4 nm that was located within the styrene block microdomains. The effects of sulfonation, nature of the cation, temperature and sample preparation on the different microstructures and the properties of the polymers were studied by dynamic mechanical analysis, transmission electron microscopy, and small angle x-ray scattering. The effect of adding homopolymers that are miscible with the ionic phase was also studied.				
14. SUBJECT TERMS Block Copolymers, Ionomers, Microstructure, Transitions, Morphology			15. NUMBER OF PAGES 7	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL	

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FINAL REPORT

Grant # N00014-56-J-0011

R&T Code: uri5302

PRINCIPAL INVESTIGATOR: R. A. Weiss

INSTITUTION: The University of Connecticut

GRANT TITLE: Synthesis and Characterization of Block Copolymer Ionomers with Coexisting Dual Microphase Separated Morphologies

AWARD PERIOD: 1 July 1991 -- 30 June 1994

OBJECTIVE: To synthesize and characterize the structure and properties of block copolymer ionomers.

APPROACH: Hydrogenated di- and triblock copolymers of styrene and a diene were either obtained from a commercial source or synthesized by anionic polymerization followed by hydrogenation of the diene block. Three types of copolymers were obtained: (1) triblock copolymers of styrene/ethylene-co-butylene/styrene (SEBS); (2) diblock copolymers of styrene/ethylene-co-propylene (SEP); and (3) triblock copolymers of styrene/ethylene-co-propylene/styrene (SEPS). The styrene content of the SEBS was 30%(wt); the styrene content of the SEP and SEPS was varied from 10-50% to accomplish block microstructures ranging from spherical to cylindrical to lamellar domains. The styrene blocks were lightly sulfonated with acetyl sulfate following the procedure of Makowski, Lundberg and Singhal (U.S. Pat. 3,870,841). Sulfonate concentration varied from 0-18 mol% of the styrene and the free acid derivative and the Na⁺ and Zn²⁺ salts were studied. The block copolymer ionomers exhibited two different levels of microphase separation: (1) a block microstructure with a characteristic dimension of the order

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styrene block microdomains. The effects of sulfonation, nature of the cation, temperature and sample preparation on the different microstructures and the properties of the polymers were studied by dynamic mechanical analysis, transmission electron microscopy, and small angle x-ray scattering. The effect of adding homopolymers that are miscible with the ionic phase was also studied.

A. WORK ACCOMPLISHED [*The number in brackets refer to publications in section B*]

Block Copolymer Synthesis [2,9,11,12]: SEBS block copolymers were obtained from Shell Development Corp. SEP and SEPS block copolymers were synthesized by anionic polymerization of styrene and isoprene followed by hydrogenation of the isoprene block. A summary of the latter diblock and triblock copolymers is given in Table 1, which includes the composition, molecular weight (all had narrow molecular weight distributions), the microstructure determined by small angle x-ray scattering (SAXS) and transmission electron microscopy (TEM), the interdomain spacing and the order-disorder transition temperature determined by dynamic mechanical analysis (DMTA).

The block copolymers were sulfonated using the procedure of Makowski, Lundberg and Singhal (U.S. Pat. 3,870,841). The sulfonating reagent was acetyl sulfate, and sulfonations were performed in homogenous solutions using dichloroethane. Sulfonate concentration varied from 0-18 mol% of the styrene and the free acid derivative and the Na^+ and Zn^{2+} salts were studied.

PS, the morphology changed from body-centered cubic packed spherical domains of PS to hexagonal packed PS cylinders to alternating PS and PEP lamella. The ODT transition was determined by DMTA, and for a fixed composition and total polymer molecular weight, the T_{ODT} for the diblocks were about twice that of the triblocks. Partial sulfonation of the PS blocks inhibited the formation of the block microstructure, but did not change the texture. The inhibition to the development of order increased as the strength of the dipolar interactions increased, i.e., in the order of cation $H < Zn < Na$. The compression molded SEP50 sample exhibited two anomalies: (1) a rheological transition between T_g and T_{ODT} that may represent an order-order transition and (2) a mixed morphology of lamella and perforated lamella microstructures as observed by TEM.

Thermally-Induced Transitions [10]: Thermally-induced morphology changes of sulfonated SEBS were investigated using time-resolved SAXS measurements. At elevated temperature, order-order and/or order-disorder transitions of the block microstructure were observed following dissociation of the ionic aggregates for the free acid and zinc salt derivatives. The critical temperature for dissociation of the ionic phase was relatively insensitive to sulfonation level, but strongly dependent on the nature of the cation. The ionic dissociation temperature was ca. 175°C for the free acids, 235-250°C for the Zn-salts and was not observed for the Na-salts. Thermally induced transitions of the block microstructure were sensitive to the sulfonation level. At low sulfonation levels (e.g., 3 mol%), the order-disorder transition of the block microstructure was lower than the ionic dissociation temperature. As a result, the order-disorder transition was

sulfonate concentrations (9 mol%), an order-order transition from a spherical to a lamellar block microstructure occurred following dissociation of the ionic aggregates. This was also accompanied by phase mixing of the blocks, which indicated that the order-disorder transition was close to, but above, the ionic dissociation temperature. At the highest sulfonation studied (18 mol%), the order-disorder transition of the block microstructure occurs at significantly higher temperature than the ionic dissociation temperature. In that case, improvements in the block microphase separation occurred above the ionic dissociation temperature.

Blends of Homopolymer with Block Copolymer Ionomers [4,6]: The incorporation of specific intermolecular interactions into a blend of a homopolymer (HP) and a block copolymer (BC) increased the miscibility of the homopolymer in the block copolymer beyond the theoretical limit for athermal HP/BC blend. Relatively polar homopolymers that can interact with the sulfonate groups, e.g., poly(vinyl pyridine) and polycaprolactone, partition preferentially into the ionomeric block of the block copolymer ionomer. In the case of blends of polycaprolactone (PC), which is a crystallizable polymer, with SEBS block copolymer ionomers, the PC swelled the ionic block and formed nano-sized crystallites within the ionomeric domains.

Significance of This Work: Block copolymer ionomers possess two different self-assembled microstructures that differ in size by an order of magnitude. The combination of two different microphases within a single polymer allows one considerable flexibility in the development and control of polymer morphology and properties. For example, judicious control of the ionic

at elevated temperatures superior to those of currently commercial styrene-based block copolymer TPEs. The block copolymer ionomers also combine hydrophobic and hydrophilic microdomains, which give them unique characteristics, such as the ability to swell different parts of the polymer with nonpolar or polar diluents -- including polymeric diluents. This property plus the ability to develop nano-size crystalline textures within a microdomain suggest that these materials may have application in technologies such as membranes, controlled release, solid-state batteries, interfacial agents or chemical or biological sensors. In addition, combination of the microstructures of an ionomer and a block copolymer allowed us to access for the first time the order-disorder transition of the ionic microstructure of an ionomer. Thus, these materials also allow one to pursue studies of ionomer physics that have been hitherto impossible.

Table 1 : Characteristics of the block copolymers studied and summary of results

Architecture	Designation	PS content, wt% ^a	M _n , daltons ^b	Morphological Characteristics		T _{ODT} , °C ^f
				Type ^{c, d}	Dimension, nm ^e	
Diblock	SEP10	10.8	48200	Spheres	24.6	180
Diblock	SEP20	20.3	54000	Cylinders	40.3	325
Diblock	SEP35	35.6	52000	Lamellae	53.2	--
Diblock	SEP50	50.4	52000	Lamellae	49.9	--
Triblock	SEPS9	9.0	54900	--	--	80
Triblock	SEPS21	21.5	49300	Cylinders	23.2	150
Triblock	SEPS50	50.8	50000	Lamellae	30.1	275

Legend : ^a : Determined through proton NMR; ^b : Determined through gel permeation chromatography (GPC);
^c : Determined by SAXS; ^d : Determined by TEM; ^e : Dimension D = 2 π /q*; ^f : Determined by DMTA

B. PUBLICATIONS

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9. Mani, S., R. A. Weiss, C. E. Williams, and S. F. Hahn. 1994. Characterization of the Block Microstructure in Block Copolymer Ionomers Using Small Angle X-Ray Scattering. *Polym. Mat. Sci. Eng.*, 71: 565-566.
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11. Mani, S., R. A. Weiss, S. F. Hahn, C. E. Williams, M. E. Cantino and L. H. Khairallah. 1995. Microstructure of Styrenic Block Copolymers and Their Sulfonated Ionomers. *Ann. Tech. Conf., Soc. of Plast. Eng.*, in press.
12. Mani, S., R. A. Weiss, S. F. Hahn, C. E. Williams, M. E. Cantino and L. H. Khairallah. 199 . Microstructure of Block Copolymers of Polystyrene and Poly(r-ethylene-co-r-propylene). *Macromolecules*, submitted.

C. Patents: None

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